Energy Disposal and Energy Consumption in Elementary Chemical Reactions: the Information Theoretic Approach

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Since the early days of chemical kinetics it has been recognized that collisions between the reacting molecules constitute the microscopic mechanism underneath the observed, bulk, macroscopic reaction process. It is, however, only recently that progress in both experimental techniques and theoretical interpretation has brought us to the point where we can probe an elementary chemical reaction directly on the microscopic, molecular level.[1-9] We are entering an era where the intimate details, the evolution of reactants to products in a single collision, can be examined by the methods of chemical dynamics.[1]

It is now possible to prepare reactants in fairly well-defined internal states and determine whether chemical reaction takes place during the single collision between them. One can thus study the role of internal energy of the reactants in bringing about a chemical rearrangement.[5] One can also select the velocity with which the reactants collide. As an illustration, the exothermic reaction[5c]

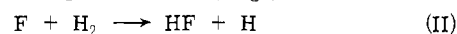$$HI + DI \longrightarrow HD + I_2 \qquad (I)$$

fails to go even when there is more than enough translational energy of the colliding molecules to overcome any activation barrier. Upon collision the two molecules simply rebound, without any chemical rearrangement taking place, when the reactants are vibrationally cold.

It is also possible to resolve the internal states[1,2,6]

(and/or the velocity[4]) of the product molecules emerging from a single collision. Very often, the internally excited nascent products of an elementary exoergic collision emit radiation (ir, visible, or uv) allowing identification of the excited product states.[2-6] As an example, consider, *e.g.*,[1]

$$F + H_2 \longrightarrow HF + H \qquad (II)$$

In a single reactive collision the H_2 bond has been replaced by the stronger HF bond. During the collision, the exoergicity is released into product translational recoil and internal energy of the newly formed HF molecule. When the reaction is studied in bulk, the nascent product molecules proceed to collide with other molecules. The transfer of energy upon these subsequent collision tends to "disperse" the exoergicity of the reaction among all the bath molecules, and the energy released in the reaction appears as heat. (In conventional terms the reaction is *exothermic*.) From a fundamental viewpoint, however, we are more concerned with the outcome of a

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(1) R. D. Levine and R. B. Bernstein, "Molecular Reaction Dynamics," Clarendon Press, Oxford, 1974.

(2) For detailed reviews, see (a) T. Carrington and J. C. Polanyi, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Phys. Chem., Ser. One,* 9, 135 (1972); (b) J. L. Kinsey, *ibid.,* 9, 173 (1972); (c) J. Dubrin, and M. J. Henchman, *ibid.,* 9, 213 (1972); (d) J. Dubrin, *Annu. Rev. Phys. Chem.,* 24, 97 (1973); (e) M. J. Molina and G. C. Pimentel, *IEEE J. Quantum Electronics,* 9, 64 (1973).

(3) R. D. Levine, "Quantum Mechanics of Molecular Rate Processes," Clarendon Press, Oxford, 1969.

(4) (a) D. R. Herschbach, *Faraday Discuss. Chem. Soc.,* 55, 233 (1973); (b) Y. T. Lee in "Electronic and Atomic Collisions," Invited Papers, VII ICPEAC, North-Holland, Amsterdam, 1971, p 357; (c) M. A. D. Fluendy and K. P. Lawley, "Chemical Applications of Molecular Beam Scattering," Chapman and Hall, London, 1973.

(5) (a) A. M. Ding, L. J. Kirsch, D. S. Perry, J. C. Polanyi, and J. L. Schreiber, *Faraday Discuss. Chem. Soc.,* 55, 252 (1973); (b) T. J. Odiorne, P. R. Brooks, and J. V. Kasper, *J. Chem. Phys.,* 55, 1980 (1971); (c) S. B. Jaffe and J. B. Anderson, *ibid.,* 51, 1058 (1969).

(6) H. W. Cruse, P. J. Dagdigian, and R. N. Zare, *Faraday Discuss. Chem. Soc.,* 55, 277 (1973).

(7) K. L. Kompa, *Top. Curr. Chem.,* 37, 1 (1973).

(8) J. D. McDonald, P. R. LeBreton, Y. T. Lee, and D. R. Herschbach, *J. Chem. Phys.,* 56, 769 (1972).

(9) R. B. Bernstein, *Israel J. Chem.,* 9, 615 (1971).

single reactive collision. Immediately after the reactive collision, before the products had time to engage in subsequent collisions, how is the reaction exoergicity partitioned?

Experiment shows that the exoergicity is never released *exclusively* into the relative translation but always goes at least partly into internal excitation of the product molecules. Often a very considerable fraction of the available exoergicity appears as internal excitation (some 67% for reaction II, for example). To accommodate this excess energy, excited internal states of the products are often preferentially formed. In reaction II the population of the $v = 2$ vibrational level of the newly formed HF is some 18 times greater than that of the ground ($v = 0$) level. The internal-state populations of the nascent products are usually found to be distributed in a non-Boltzmann way, often with "excess" population of higher states. This "population inversion" is the basis for chemical laser[1,7] action.

We can thus characterize energy disposal by the statement that elementary exoergic reactions are usually highly *specific* in their mode of energy release.

Just as the exoergic elementary reactions show specificity in their energy partitioning, so the reverse (endoergic) reactions exhibit a high degree of *selectivity* in their mode of energy consumption. Consider the time evolution of reactants to form products in an exoergic reaction with a quite specific pattern of energy release. Now reverse the direction of time. The "products" will now collide and evolve to form the "reactants." In so doing, the disposed exoergicity of the forward reaction is being consumed to overcome the energy barrier of the reverse (necessarily endoergic) reaction. If the "forward" reaction leads to products with high internal excitation, then microscopic reversibility[3] implies that the "reversed" reaction proceeds more readily when the energy is in the internal degrees of freedom of the reactive molecules rather than in relative translation.

It is not just the total available energy which determines the reaction probability. It becomes important to determine how and why the system is selective in utilizing different modes of energy. A fairly general characteristic of elementary reactions can be stated as: *specificity* of energy release and *selectivity* of energy consumption.

When chemical reactions are studied in the bulk under conditions which ensure thermal equilibrium (*e.g.*, an excess buffer gas, low reaction rate), the effects we are considering are not readily evident. Energy-transfer collisions rapidly repopulate any internally excited reactant levels which are depleted because of their enhanced reactivity. Similarly, such collisions rapidly equipartition any energy excess (or deficiency) in the reaction products. In the limit when the energy transfer is very much faster than the reaction rate (the limit of thermal equilibrium), selectivity of consumption (or specificity of disposal) is lost. Such "dynamic" effects are only evident in bulk systems when the reaction rate competes with the rate of relaxation to thermal equilibrium. This competition will be particularly important in those kinetic situations where the products of one elementary exothermic reaction are the reactants of a sub-

sequent reaction. The overall kinetic behavior of the system may then be very different from that expected on the basis of bulk macroscopic rate constants determined for reactants in thermal equilibrium.

This prevalence of disequilibrium is especially well known in shock-tube experiments[10,11] and in flame, combustion, and explosion kinetic studies.[12] A very important newcomer is the kinetic study of processes in chemical laser cavities.[7,13,14] To handle such disequilibrium systems we must learn how to deal with the nonequilibrium internal-state population distribution. A knowledge of the microscopic rate constants (*i.e.*, the reaction rate for the reagents in different internal states) and not just their thermal average (*i.e.*, the overall, bulk rate) is necessary in order to predict the kinetic behavior of fast reacting systems in the bulk gas phase.[9]

In view of the current (*e.g.*, chemical lasers[7]) and potential (*e.g.*, isotope separation,[15] selective synthetic pathways) practical applications[9] of chemical reactions in disequilibrium systems, one obviously would like to construct a framework for the discussion and interpretation of such phenomena. The detailed experiments under single-collision conditions are also of considerable theoretical interest.

The primary output of modern molecular collision computations[3,16,17] are the detailed, state-to-state reaction rates or cross sections. (Recall that on the microscopic level the reaction rate coefficient k is related to the reaction cross section σ_R by $k = \langle v \sigma_R \rangle$ where v is the relative velocity of the colliding reactants.[1]) The dynamical computations may be based upon quantum scattering theory[3,16,17] or the classical mechanical trajectory (Monte Carlo) method[18] or, more recently, semiclassical approaches,[19] employing *ab initio* or semiempirical potential surfaces.[1,18] The interrelation between the detailed cross sections and their energy dependence and the topology of the potential energy surface(s) (which in turn depends upon the electronic structure of the reactants, products, and the combined system) is a central question in the field of modern chemical reaction dynamics.[1,17,18]

The effort involved in acquiring so much detailed dynamical information on elementary chemical reactions is great, but so are the rewards in terms of understanding. However, there is still another price to be paid for this wealth of detail, and that is the very task of digesting it, of assimilating it, of compacting

(10) E. V. Stupochenko, S. A. Losev, and A. I. Osipov, "Relaxation in Shock Waves," Springer-Verlag, New York, N.Y., 1967.

(11) H. O. Pritchard, *Can. J. Chem.*, 51, 3152 (1973).

(12) See, *e.g.*, R. L. Fristrom and A. A. Westenberg, "Flame Structure," McGraw-Hill, New York, N.Y., 1965.

(13) M. J. Berry, *J. Chem. Phys.*, 59, 6229 (1973).

(14) A. Ben-Shaul, G. L. Hofacker, and K. L. Kompa, *J. Chem. Phys.*, 59, 4664 (1973).

(15) C. B. Moore and P. F. Zittel, *Science*, 182, 541 (1973).

(16) R. A. Marcus, *Faraday Discuss. Chem. Soc.*, 55, 9 (1973).

(17) (a) R. G. Gordon, *Methods Comput. Phys.*, 10, 81 (1971); (b) J. C. Light, *Advan. Chem. Phys.*, 19, 1 (1971); (c) R. D. Levine, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Theor. Chem.*, Ser. One, 1, 229 (1972); (d) T. F. George and J. Ross, *Annu. Rev. Phys. Chem.*, 24, 263 (1973).

(18) (a) M. Karplus in "Molecular Beams and Reaction Kinetics," C. Schlier, Ed., Academic Press, New York, N.Y., 1970, p 372; (b) D. L. Bunker, *Methods Comput. Phys.*, 10, 287 (1971); (c) P. J. Kuntz in ref 4b, p 427; (d) J. C. Polanyi and J. L. Schreiber in "Kinetics of Gas Reactions," H. Eyring, W. Jost, and D. Henderson, Ed., Academic Press, New York, N.Y., 1974.

(19) (a) R. A. Marcus, *Faraday Discuss. Chem. Soc.*, 55, 34 (1973); (b) W. H. Miller, *Advan. Chem. Phys.*, 25, 63 (1974).

it, of systematizing it. To cope with this overwhelming body of microscopic data, the use of information theory[20] would appear to be a natural approach. The purpose of this Account is to show the role which information-theoretic methods have played in dealing with the ever-increasing body of experimental and theoretical results in the field of molecular reaction dynamics.[21-36]

The Product State Population Distribution: Surprisal

The energetics and vibrational energy disposal of the elementary exoergic reaction

$$Cl + HI \longrightarrow I + HCl \qquad (III)$$

are shown in Figure 1. To account for the population of the different vibrational levels of HCl, one could argue that this is just a question of solving the dynamical equations of motion on an appropriate potential energy surface. While such computations are now feasible (at least at the level of classical mechanics on a single potential energy surface[18]) they cannot, in themselves, provide a qualitative interpretation of the results. For this purpose, let us first consider what features of the distribution shown in Figure 1 could have been expected *a priori*.

The total energy E of the colliding molecules is a conserved quantity (constant throughout the collision) and a very important variable.[1,21,27] It thus determines which states of the products are allowed to be populated. The total energy E is usually defined with respect to the lowest possible energy state (of either reactants or products) as shown in Figure 1. For a particular initial reactant state the total energy is the sum of the internal energy of the reactants, their relative translational energy, and the (zero-point to zero-point) exoergicity, $-\Delta E_0$, of the reaction. After the reactive collision the energy is partitioned between the products' internal energy and translational energy (T). If the products are an atom and a diatomic molecule, this internal energy

(20) (a) C. E. Shannon and W. Weaver, "Mathematical Theory of Communication," University of Illinois Press, Urbana, Ill., 1949; (b) A. J. Khinchin, "Mathematical Foundations of Information Theory," Dover Publications, New York, N.Y., 1957; (c) E. T. Jaynes, "Statistical Physics," Brandeis Lectures, Vol. 3, W. A. Benjamin, New York, N.Y., 1963, p 81; (d) R. Ash, "Information Theory," Interscience, New York, N.Y., 1965; (e) A. Katz, "Principles of Statistical Mechanics: The Information Theory Approach," W. H. Freeman, San Francisco, Calif., 1967.

(21) R. B. Bernstein and R. D. Levine, *J. Chem. Phys.*, **57**, 434 (1972).

(22) A. Ben-Shaul, R. D. Levine, and R. B. Bernstein, *Chem. Phys. Lett.*, **15**, 160 (1972).

(23) G. L. Hofacker and R. D. Levine, *Chem. Phys. Lett.*, **15**, 165 (1972).

(24) A. Ben-Shaul, R. D. Levine, and R. B. Bernstein, *J. Chem. Phys.*, **57**, 5427 (1972).

(25) R. D. Levine, B. R. Johnson, and R. B. Bernstein, *Chem. Phys. Lett.*, **19**, 1 (1973).

(26) A. Ben-Shaul, *Chem. Phys.*, **1**, 244 (1973).

(27) R. D. Levine, "Proceedings of the International Symposium on Chemical and Biochemical Reactivity," Academy of Science, Jerusalem, 1973, p 317.

(28) R. D. Levine and R. B. Bernstein, *Faraday Discuss. Chem. Soc.*, **55**, 100 (1973).

(29) R. D. Levine and R. B. Bernstein, *Chem. Phys. Lett.*, **22**, 217 (1973).

(30) R. D. Levine, Report WIS-TCI-495; Invited Papers, VIII ICPEAC, Belgrade, Yugoslavia, 1973, p 567.

(31) R. D. Levine, *Ber. Bunsenges Phys. Chem.*, **78**, 111 (1974).

(32) C. Rebick, R. D. Levine, and R. B. Bernstein, *J. Chem. Phys.*, **60**, 4977 (1974).

(33) A. Ben-Shaul and G. L. Hofacker in "Handbook of Chemical Lasers," J. F. Bott and R. W. Gross, Ed., Wiley, New York, N.Y., in press.

(34) R. D. Levine and R. Kosloff, *Chem. Phys. Lett.*, **28**, 300 (1974).

(35) R. D. Levine and R. B. Bernstein, *Chem. Phys. Lett.*, in press.

(36) R. D. Levine and O. Kafri, *Chem. Phys. Lett.*, **27**, 175 (1974).

Figure 1. Schematic drawing of reactant and product diatomic potentials, energy levels, and product vibrational-energy distribution for reaction III. Here $E - E_V - E_T$ is the energy which goes into rotation of the HCl product molecule.

is the sum of the vibrational (V) and rotational (R) energy of the diatom, $E = T + (V + R)$.

An immediate consequence of the conservation of energy is that the highest allowed vibrational state v of HCl is determined by the condition $V \leq E$. We can express this restriction in a more natural way[1,27] by considering the ratio $f_V = V/E$, the fraction of the available energy partitioned into the vibration of the products. Clearly, f_V is restricted to be in the range of 0 to 1, irrespective of the magnitude of E or, for that matter, of an isotopic substitution (*e.g.*, replacing HI by DI so that the product is DCl). In a similar fashion we can introduce the fractions $f_T = T/E$ and $f_R = R/E = 1 - f_V - f_T$.

Thus we are not surprised to find that for all the vibrational states of the products $0 \leq f_V \leq 1$. But how surprised are we at the individual state populations? Is it very surprising that the $v = 3$ state of HCl in Figure 1 is the level most heavily populated by the reactive collision, or should we have expected that, *a priori*? To answer this question we must clarify two points. First, what are our prior expectations, and second, what constitutes a measure of our surprise?

A quantitative measure of the "surprisal" of an outcome has been proposed by Claude Shannon in 1948, in his fundamental paper on information theory.[20] We can recast his argument as follows. Let A and B be two independent events and let $I(A)$ and $I(B)$ be the surprisals associated with observing events A and B, respectively. Suppose that we observed the occurrence of both A and B. Since they are independent events, our observation that event A has happened in no way changes our expectations about event B. Hence, it is reasonable to impose the condition that our surprise at the combined event (both A and B) be the sum of the surprisals at each individual event (eq 1). The definition of the surpri-

$$I(A \text{ and } B) = I(A) + I(B) \qquad (1)$$

sal should also be such that, the more probable the event, the less surprised we are at observing it. This implies that the surprisal, $I(A)$, should be a monotonically decreasing function of the probability, $P(A)$, of the event A. These two conditions are sufficient to obtain Shannon's original definition. We recall that if A and B are independent events, $P(A \text{ and } B) = P(A)P(B)$. It then follows from the above that $I(A)$ varies logarithmically with $P(A)$. Specifically

$$I(A) = -\ln P(A) \qquad (2)$$

The definition above is not quite sufficient for our purpose. The events we wish to consider (say, the re-

active collision yielding a given vibrational level of HCl) are not elementary events, but can be realized in a large number of ways. As an example, consider many repetitions of the experiment consisting of tossing two coins. In a large number of trials we will observe that the outcome "the two faces are different" occurs more frequently than the events "both heads" or "both tails." Yet, we do not find this result surprising. Our *a priori* expectations are that a fair coin toss will yield either heads (H) or tails (T), with equal probability, unless the coin is biased. In the combined experiment the possible outcomes are then HH, HT, TH, and TT (with equal probability, in the absence of bias). The event "the two faces are different" is more probable simply because it corresponds to two possible elementary outcomes (HT and TH). We are *a priori* prepared for this event being more probable, and are thus not surprised when our *a priori* expectations are realized. In other words, $-\ln P(A)$ corresponds to our intuitive notion of a surprisal only when all observed events are, *a priori*, equally probable. When this is not the case, we must assign to each event its prior probability, $P^0(A)$. This prior distribution should reflect any *a priori* information we may have about the distribution of outcomes. In particular, as shown by our coin tossing example, the prior probability is a measure of the number of (equally probable) elementary events that correspond to the outcome in question.

We thus define the surprisal as the difference between the post and prior values[21,27,30]

$$I(A) = -\ln P(A) - [-\ln P^0(A)] = -\ln [P(A)/P^0(A)] \quad (3)$$

If the event A occurs with the same probability as initially expected (*i.e.*, $P(A) = P^0(A)$), then we are not surprised ($I(A) = 0$).

The surprisal $I(A)$ is then a measure of the deviation of the observed probability $P(A)$ from the *a priori* expected probability $P^0(A)$, such that

$$P(A) = P^0(A) \exp[-I(A)] \quad (4)$$

Rather than reporting the probability of the event one can report its surprisal, its deviation from expectation. (But to characterize a distribution, we still need as many different surprisals as the number of possible events!)

Let us apply these ideas to the distribution of product vibrational states. First we need to specify the *a priori* distribution. At a given value of the total energy, and in the absence of additional prior information, all possible products' quantum states can be assumed to be equally probable. The physical rationale for this assumption is that during a reactive collision the molecules undergo severe rearrangements and deformations, and since considerable energy is involved, strong selection rules are unlikely, so that all final quantum states would be expected to be roughly equiprobable. The assumption that all conservation-allowed final products' quantum states are equally probable is the basis of a statistical model of reaction rates. However, here the statistical model is used only to compute the distribution in the absence of prior information. We then compare the observed with this *a priori* distribution in order to obtain the surprisal.

The prior expected distribution of product states is thus to be computed from the assumption that all final quantum states of the products (at a given energy) are populated with equal probability. Now, if the product diatom is in the vibrational state v, the energy $E - V$ is available for partitioning among the rotation of the diatomic molecule and the relative translation of the atom and the diatomic molecule. The smaller the v, the more energy is available to populate the rotational and translational states. There are more quantum states of the products that can be populated for low than for high v (at a given energy).

A very simple calculation provides a more quantitative description. The number of quantum states (per unit volume) when the translational energy is in the range T to $T + dT$ is[3,37] $A T^{1/2} dT$, where A is a combination of constants. Hence the number of quantum states (per unit volume) of the products when the diatomic molecule is in the vibrational level v and rotational level J and the translational energy is in the range T to $T + dT$ is $(2J + 1)A T^{1/2} dT$, where $(2J + 1)$ is the degeneracy of the level J. Consider a model of the diatomic as a harmonic oscillator–rigid rotor[24,37] (RRHO). The rotational energy $R = BJ(J + 1)$ can often be regarded as a continuous variable. The number of available quantum states when the diatomic is at the level v and the total energy is E can be obtained by integrating over all values of R and T such that $R + T = E - V$.

$$\int dR \int dT A' T^{1/2} \delta(E - V - R - T) =$$

$$A' \int_0^{E-V} dR (E - V - R)^{1/2} = A''(E - V)^{3/2} \quad (5)$$

Here A' and A'' are combinations of constants. Since $P(f_V) = P(V)(dV/df_V)$, we obtain[24]

$$P^0(f_V) = (5/2)(1 - f_V)^{3/2} \quad (6)$$

A more exact treatment of the energy levels somewhat modifies the functional dependence on f_V, but the major qualitative prediction of this equation is unchanged: *a priori*, $P^0(V)$ is a *decreasing* function of V. Thus, in the absence of any dynamic bias, a considerable fraction of the exoergicity is released as translation. The observation that this is not necessarily so indicates that the distribution of the vibrational states of products is not really statistical but is somehow constrained by the dynamics.

Having decided upon the *a priori* distribution $P^0(V)$, we can evaluate the surprisal of the observed populations (eq 7). A plot of the vibrational surprisal

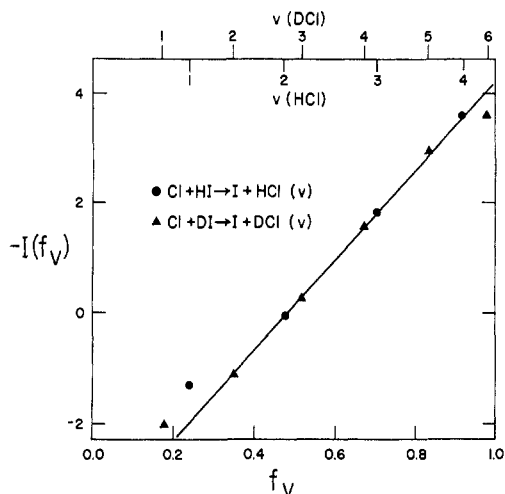$$I(f_V) = -\ln [P(f_V)/P^0(f_V)] \quad (7)$$

vs. f_V can reveal the trends in the "deviation from expectation" as a function of the degree of vibrational excitation of the product.

As an illustration of the analysis of vibrational population inversions, we show a number of surprisal plots derived from the literature.

Figure 2 shows the results for the reaction F + HBr → HF(v) + Br. Plotted are the observed rela-

(37) J. L. Kinsey, *J. Chem. Phys.*, 54, 1206 (1971).
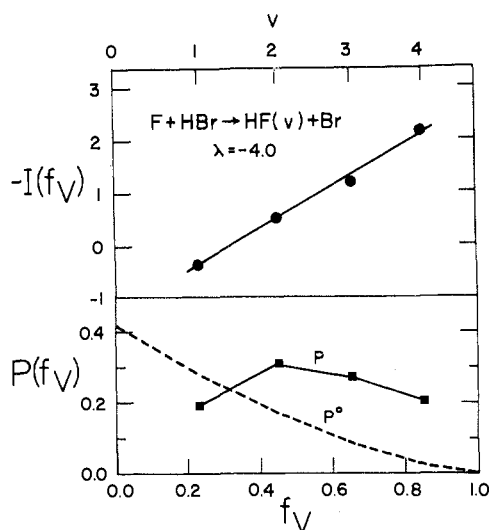
Figure 2. Surprisal analysis[24,26] of the product vibrational-state distribution of the F + HBr reaction. The upper abscissa scale is v, the lower scale f_V. Lower panel: comparison of the observed final vibrational-state population (P) with the prior expectation (P^0). Upper panel: vibrational surprisal plot.
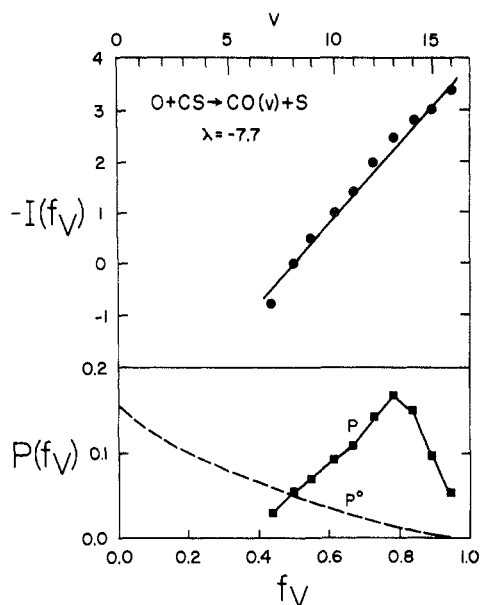

Figure 4. Surprisal analysis of a nonhydrogenic reaction. (Plot similar to Figure 2.) The vibrational spacings are narrower and many more levels can be populated; the surprisal plot is essentially linear.

Figure 3. Vibrational surprisal plot[22] for the pair of isotopic reactions Cl + HI (DI) → I + HCl (DCl).

tive populations $P(v)$ [or $P(f_V)$], and the prior (*i.e.*, not surprising) populations $P^0(v)$ (assuming the rotating-vibrator approximation[24] for the density of states of HF). The ratio $\omega(f_V) \equiv P(f_V)/P^0(f_V)$ is found to be a smooth function of f_V. The vibrational surprisal $I(f_V) \equiv -\ln \omega(f_V)$ is plotted *vs.* f_V, and from the slope of the straight line the vibrational-temperature parameter λ_v ($\lambda_v = dI(f_V/f_V)$ is found to be -4.0.

Figure 3 shows analogous results for the isotopically related reactions (III): Cl + HI → HCl(v) + I and Cl + DI → DCl(v) + I. There is a significant difference in the product vibrational state distributions for the two isotopic reactions. However, the vibrational surprisal plots have essentially the same slope, yielding $\lambda_v = -8.0$. Similar results obtain for the isotopic reactions F + H₂, F + D₂, and F + HD. The slopes of the vibrational surprisal plots are nearly constant, but there are small differences between the results for the HF-producing *vs.* the DF-producing reactions.[13,38]

(38) M. J. Berry, *Chem. Phys. Lett.*, **27**, 73 (1974).

Figure 4 shows analogous results for a nonhydrogenic system, the population-inverting reaction: O + CS → CO(v) + S. The surprisal is seen to be a near-linear function of the fraction f_V as before. The population inversion can be characterized by the large (negative) λ_v value from the slope of the surprisal plot $I(f_V)$.

Although linear surprisals are found for many reactions, this is not a completely general finding. A notable exception is the reaction type H + X₂ → HX + X (where X = halogen and D may replace H), for which vibrational surprisal plots are found to be nonlinear.[24] (Even so, the variation of the surprisal with f_V (or with the total energy E) is much simpler (and more systematic) than the variation of the populations themselves.)

On the basis of the preceding discussion, it is evident that, while $P(V)$ has an entirely different character from $P^0(V)$, the surprisal can often be well approximated by a simple linear equation

$$P(V) = P^0(V) \exp(-\lambda_v f_V)/\exp(\lambda_0) \qquad (8)$$

Since $P^0(V)$ is a decreasing function of f_V, it follows that λ_v must be negative. Note that $\lambda_v = dI(f_V)/df_V$ is a differential measure of the deviation of the observed distribution $P(V)$ from the *a priori* expected distribution $P^0(V)$. A given value of λ_v is sufficient to characterize the entire f_V dependence of $P(V)$. In this sense, λ_v plays the role of a temperature-like parameter. Population inversion corresponds to a negative value of λ_v.

We also note that $\exp(\lambda_0)$ plays the role of a partition function.

$$Q_v = \exp(\lambda_0) = \sum_v P^0(V) \exp(-\lambda_v f_V) \qquad (9)$$

The average value of f_V is

$$\langle f_V \rangle = \sum_v f_V P(V) = -d \ln Q/d\lambda_v \qquad (10)$$

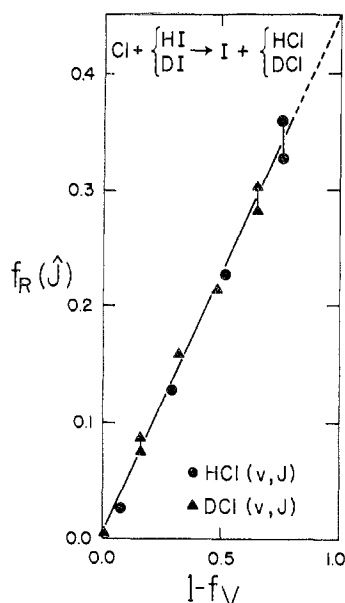This illustrates the formal role of $\exp(\lambda_0)$ as the par-

Figure 5. Plot[25] of the dependence of the most probable rotational energy disposal $(f_R(J))$, in a given vibrational manifold, *vs.* $1 - f_V$ for the pair of isotopic reactions of Figure 3.

tition function and of λ_v^{-1} as a temperature-like parameter.

The method of chemiluminescence[2a] can determine not only the populations of the different *vibrational* levels but also the population of the different *rotational* levels within any given vibrational manifold. This is a conditional distribution, *i.e.*, a distribution of rotational energy for a given amount of vibrational energy, which we shall denote as $P(R|V)$. Since V is given, the available energy for rotational excitation is anywhere from 0 up to $E - V$. The natural reduced variable (fraction of available energy in rotation) would then be[25,27]

$$g_R \equiv R/(E - V) = f_R/(1 - f_V) \qquad (11)$$

We thus expect that when $P(R|V)$ is expressed in terms of g_R, the distribution would be independent of either the particular vibrational manifold or of isotopic substitution.

A qualitative examination of known results for $P(R|V)$ confirms that it appears to be a function of g_R only, for all the vibrational manifolds of a given reaction. A more quantitative test is to determine the most probable rotational level (say J) in each vibrational manifold. The rotational energy of this level should be a linear function of $E - V$. Figure 5 shows[25] a plot of $f_R(J)$ *vs.* $1 - f_V$ for the pair of isotopic reactions Cl + HI (DI) → I + HCl (DCl), confirming this expectation.

For a detailed analysis of the distribution of the population of the rotational levels we need to examine the (conditional) surprisal

$$I(R|V) = -\ln [P(R|V)/P^0(R|V)] \qquad (12)$$

where, since V is given and R is specified

$$P^0(R|V) \propto f_T^{1/2} = (1 - f_V - f_R)^{1/2} =$$

$$(1 - f_V)^{1/2}(1 - g_R)^{1/2} \qquad (13)$$

In the simplest case, *i.e.*, a linear "rotational surprisal"

$$I(R|V) = \text{const} + \theta_R g_R \qquad (14)$$

or

$$P(R|V) = P^0(R|V) \exp(-\theta_R g_R)/Q_{Rv} \qquad (15)$$

Here Q_{Rv} is a normalizing factor. Thus the joint vibrotational population distribution becomes

$$P(R, V) = P(R|V)P(V) =$$

$$P^0(R|V)P^0(V) \exp(-\lambda_v f_V - \theta_R g_R)/Q \qquad (16)$$

The analysis of available experimental results[25] has consistently yielded quite small values of θ_R, *i.e.*, rotational energy distributions are "not very surprising." [25,26] (This means that $P(R|V)$ is quite close to $P^0(R|V)$.) Thus it is a reasonable approximation to take all rotational quantum states within a given vibrational manifold to be equally probable. In the language of statistical mechanics, the rotational states are essentially in "microcanonical equilibrium."

Thus far we have centered attention on the analysis of the product *internal* energy states. But molecular beam techniques[1,4,8] often provide directly the products' *translational* (recoil) energy distributions. By analogy to the linear surprisal plots found for the internal state distributions, we may expect the translational distribution to be of the form[24,28,39]

$$P(f_T) = P^0(f_T) \exp(-\lambda_T f_T)/Q_T \qquad (17)$$

or

$$I(f_T) = \lambda_0 + \lambda_T f_T \qquad (18)$$

For the prior (or reference) distribution $P^0(f_T)$, the RRHO approximation provides the result

$$P^0(f_T) = (15/4)f_T^{1/2}(1 - f_T) \qquad (19)$$

This corresponds to taking an "analytic approach." We can employ an alternative, synthetic, scheme,[25,26,28] generating the translation-energy distribution from the vibrotational-energy distribution. Since $T = E - V - R$, $P(T) = \int dV \int dR\, P(V,R)\delta(E - T - V - R)$. In the RRHO approximation, and in the limit when $\theta_R \to 0$ and λ_V is not too negative, one can show analytically that $\lambda_T \approx -\lambda_v/2$. In other words, reactions which lead to population inversion and thus negative λ_v will have positive values of λ_T.

Finally, we note that the population distribution under analysis need not come from a reactive collision. It is possible (*e.g.*, by laser excitation) to selectively populate a particular vibrotational level of a molecule. One can then observe the distribution of final states which result when such a molecule collides with an inert partner. Figure 6 shows a suprisal analysis[40] of the final vibrational energy V' when an I_2 molecule (in a state of given vibrational energy V) is deactivated by a collision with a rare gas atom.

For the sake of brevity we have omitted consideration of the surprisal associated with energy *consumption* nor have we dealt with the interrelation between the reactant energy states and the resulting product state distribution,[28,32] nor their variations with total energy. We refer the interested reader to the literature.[21-36]

(39) D. L. King, H. J. Loesch, and D. R. Herschbach, *Faraday Discuss. Chem. Soc.*, 55, 222 (1973).
(40) M. Rubinson and J. I. Steinfeld, *Chem. Phys.*, 4, 467 (1974).

Table I
Measures of Specificity of Energy Disposal[24]

Reaction Source	Cl + HI → I + HCl		Cl + DI → I + DCl	
	Exptl	Trajec-tories	Exptl	Trajec-tories
E, kcal mol^{-1}	34.0	34.0	34.0	34.0
$\langle f_v \rangle$	0.71	0.74	0.71	0.72
λ_v	−8.0	−8.4	−8.0	−8.4
$\Delta S^{(vib)}$, eu	3.66	4.03	3.66	3.90

The Thermodynamic Approach

The surprisal is a measure of the deviation of a particular population from the prior (or reference) value. One can also seek a measure for the average value (over the entire distribution) of this deviation. It turns out that the average value of the surprisal is known as the entropy[20,21,24] of the distribution. Using, as an example, the population of vibrational levels, we obtain $S^{(vib)}$, the entropy of the vibrational population, as

$$S^{(vib)} = -R \sum_v P(V) \ln [P(V)/P^0(V)] \quad (20)$$

where R is the gas constant.

It follows from the inequality $\ln X \leq X - 1$ that $S^{(vib)} \leq 0$, with equality for $P(V) = P^0(V)$. We can thus define an entropy *deficiency* as the nonnegative quantity

$$\Delta S^{(vib)} = S^{0(vib)} - S^{(vib)} = R \sum_v P(V) \ln [P(V)/P^0(V)] \quad (21)$$

Here $S^{0(vib)}$ is the value when $P = P^0$. Table I is a summary of the results of such an analysis for the Cl + HI (DI) reactions. The extensive vibrational population inversion in these reactions is reflected both by the large negative value of λ_v and the large entropy deficiency. As expected, both λ_v and $\Delta S^{(vib)}$ are essentially the same for different isotopic variants of the same reaction.

The entropy deficiency provides a compact numerical measure of the average deviation of the observed distribution from the prior (or reference) expectation. Moreover, this measure is independent of whether the surprisal plot is linear or not. It is well defined for all situations, and the larger its magnitude the more extensive is the deviation from the prior (or, microcanonical) distribution. The entropy deficiency provides us also with an important conceptual tool. To see this we need to examine briefly the concept of a thermodynamic weight.[29]

Consider an event which has several (say, n) different possible outcomes and which is repeated N times. Let N_i be the number of trials which resulted in the ith outcome, $i = 1, \ldots, n$. In principle, any set of numbers N_i such that $N = \sum_i N_i$ is a possible distribution of outcomes. However, as $N \to \infty$ one particular distribution (*i.e.*, a particular set of numbers, N_i) becomes much more probable. It can be shown that this is the distribution of maximal thermodynamic weight. In the limit $N \to \infty$ the thermodynamic weight W can be expressed as [29-31]

$$W = W^0 \exp(-N\Delta S/R) \quad (22)$$

Here W^0 is the weight when all outcomes are equally
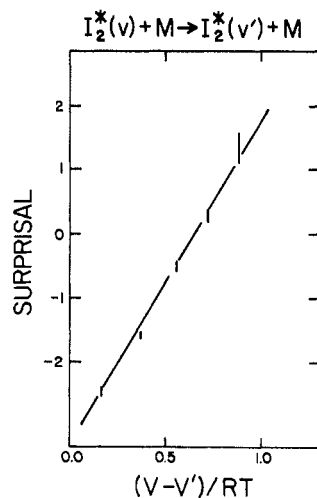
Figure 6. Surprisal plot[40] for the vibrational deactivation of I_2^* ($v = 43$) by rare gas atoms. The surprisal is plotted *vs.* the energy transfer in the collision in units of RT (where T is the temperature, K). The bars indicate the range of values for different rare gas atoms. The surprisal (and its slope) is essentially independent of the mass of the deactivating atom.

probable, and ΔS is the entropy deficiency of the distribution.

Thus, when an event is repeated a large number of times, only one particular distribution of outcomes will be observed, the one corresponding to maximal thermodynamic weight. If all outcomes are equally probable, this will be W^0. If not, this will be the distribution with the *smallest possible* entropy deficiency. Moreover, in the limit of large N the distribution of minimal ΔS will be overwhelmingly favored. (This maximal entropy principle is taken as an axiom in the Jaynes approach[20c,e] to statistical mechanics.)

In any molecular dynamics experiment one examines many independent single collisions. We thus conclude that the observed population distribution of the products will be the one with the minimal entropy deficiency. This does not imply, however, that invariably the observed population distribution equals the prior distribution (so that $\Delta S = 0$). The molecular dynamics can introduce constraints which imply nonzero surprisals and hence nonvanishing entropy deficiency. What it does imply is that, among all the possible distributions which are consistent with the dynamic constraints, the one which will be observed is the one with minimal entropy deficiency.

To apply this principle one can take either of two complementary paths. One is the synthetic route where we predict the distribution on the basis of *assumed* dynamic constraints, deduced from a detailed analysis[23] of the dynamics or based on a simple physical model[27] (or even on the basis of speculation[26]). The technical details of implementing this procedure have been extensively discussed in the literature.[23,27]

The complementary approach is the analytic one.[29,30] An experiment measuring the population distribution has just been performed. What do the results imply? How much information about the dynamics have we gained?

We assume that the surprisal can be represented by a series in f_V, e.g.

$$I(f_V) = \lambda_0 + \sum_{m=1} \lambda^{(m)} f_V^m \quad (23)$$

The coefficients $\lambda^{(m)}$ can be determined by fitting (23) to the experimental distribution. To each coefficient there corresponds a "moment"

$$\langle f_V{}^m \rangle = \sum_v f_V{}^m P(f_V) \qquad (24)$$

Using the principle of minimal entropy deficiency one can show that the only coefficients $\lambda^{(m)}$ which are nonvanishing are those for which the moments are independent pieces of information. (Two moments, $\langle f_V{}^m \rangle$ and $\langle f_V{}^n \rangle$ are independent if knowledge of one is not sufficient to compute the other.)

As an example, consider the common case of a linear vibrational surprisal (*i.e.*, where only the $m = 1$ term in (23) contributes). Then all higher moments $\langle f_V{}^m \rangle$, $m > 1$ (and hence the expectation value of any function of f_V) are determined by $\langle f_V \rangle$. This is readily evident: if the surprisal plot is linear, and we thus know λ_v, we can generate the entire distribution (using, say, (17)) and hence compute any other moment (from (24)) or any other expectation value.[29]

Another useful application of the criterion of minimal entropy deficiency is the determination of branching ratios[34,35] for competing reaction paths. Consider, for example[41]

$$F + HD \longrightarrow \begin{cases} FH + D & \text{(IVa)} \\ FD + H & \text{(IVb)} \end{cases}$$
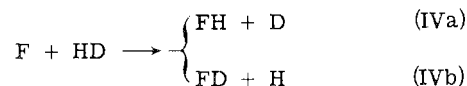
One can show that the branching ratio Γ_{ab} (here, an intramolecular isotope effect) is related to the difference in the entropy deficiency between reactions a and b. One expects that at higher collision energies the branching ratio should be approximated by its prior value, $\Gamma_{ab}{}^0$ (which can be computed on the basis of simple statistical considerations).

Concluding Remarks

The information-theoretic approach has made possible the compaction of data in the fields of molecular beam kinetics, chemiluminescence, and chemical lasers.

(41) R. B. Bernstein and R. D. Levine, *J. Chem. Phys.*, in press.

The surprisal analysis of vibrational population inversions often leads to a one-parameter description of the disequilibrium in fast, exoergic, elementary reactions. This is of importance in characterizing the gain in chemical lasers.[14,33,36] Formerly an ill-defined "vibrational temperature," T_{vib} had been used for this purpose. However, there were a number of well-known difficulties associated with its use (*e.g.*, a different T_{vib} was needed for each v state!). It is more reasonable to express gain factors and lasing conditions in terms of λ_v instead of such T_{vib}'s.

An important aspect of the thermodynamic point of view is the use of the entropy as a state function, in the classical thermodynamic sense.[30,36,42] For example, one can evaluate the entropy cycle associated with the operation of a laser[36,43] (of which the chemical laser is a special case). This has considerable bearing on the efficiency and other operational characteristics of the laser, a matter of some technical importance.[9,33]

When one combines the measures of the specificity of energy disposal, the selectivity of energy consumption, and the propensity of energy transfer, one has a complete summary of the behavior of the system far from equilibrium.

Of course, the most fundamental "practical" application is the simplification in the description of severely nonequilibrium state distributions. The key to the approach is the concept of the surprisal, the *deviation* from expectation on the basis of microcanonical equilibrium. Clearly the deviation is a more smoothly varying function of the classical energy variables than the populations themselves; therein lies the practical advantage of the present approach.

(42) A. Ben-Shaul, *Mol. Phys.*, 27, 1585 (1974).
(43) R. D. Levine and O. Kafri, *Phys. Rev.*, in press.